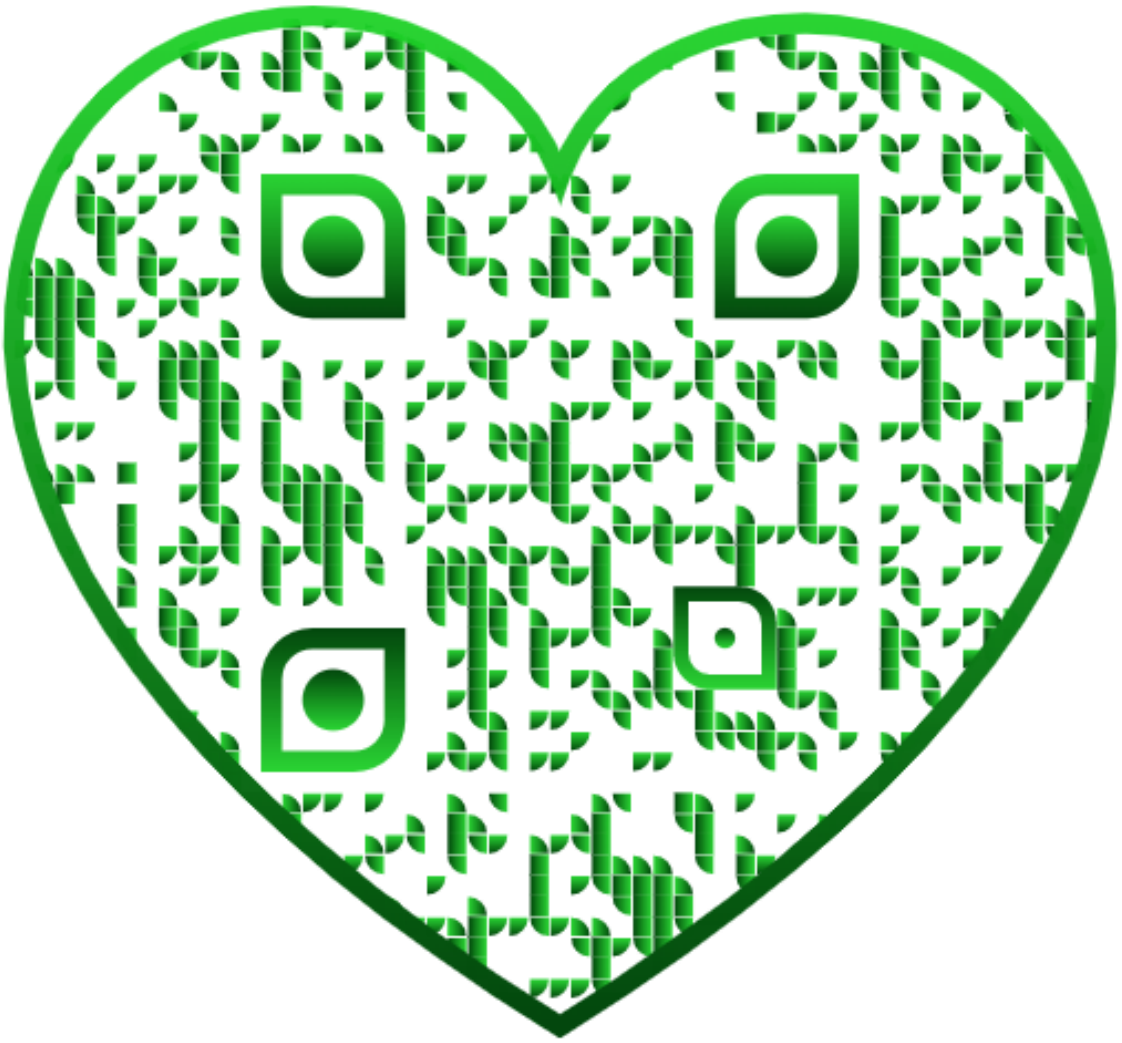
2. Phase Equilibria

- **Intermolecular forces of interaction**
- **The phase rule**
- **Phase equilibria of single, two and three component systems**



Intermolecular forces

- Whether or not a substance dissolves in a given system and the extent to which it dissolves depend largely on:
  - The nature and intensity of the forces present in the solute, the solvent, and
  - The resultant solute-solvent interaction.
- The nature of these interaction energies determines the solubility of substances in various classes of solvents.

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- The term 'intermolecular forces' is used to describe all the forces, both attractive and repulsive, between groups of neutral molecules or atoms.

- Forces between atoms within a molecule ('intramolecular forces') are usually called **chemical bonds**.

- Intermolecular forces are caused by the attractions and repulsions between the charged particles that make up the atoms in molecules.

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- Types of intermolecular forces:
  - Dipole – Dipole Forces
  - Ion – Dipole Forces
  - Dipole – Induced dipole Forces
  - Ion – Induced dipole Forces
  - Dispersion Forces (London dispersion forces/Van de Waals forces)
  - Hydrogen Forces

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Dipole – Dipole Interactions

- Molecular dipoles occur due to the unequal sharing of electrons between atoms in a molecule.
  - Those atoms that are more electronegative pull the bonded electrons closer to themselves.
  - This buildup of electron density around one of the atoms resulting in a molecular dipole.
    - One side of the molecule possesses a partially negative charge and the other side a partially positive charge.

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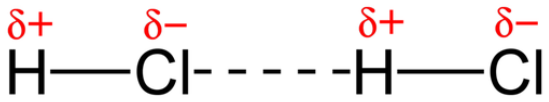
- Dipole-dipole forces are attractive forces between the positive end of one polar molecule and the negative end of another polar molecule.

E.g. Intermolecular force that contributes to the condensation of hydrogen chloride to a liquid at low temperatures.



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Ion – Dipole Interactions

- An ion-dipole force is an attractive force that results from the electrostatic attraction between an ion and a polar molecule.
- Most commonly found in solutions.
  - Especially important for solutions of ionic compounds in polar liquids.
- Ion-dipole attractions become stronger as either the charge on the ion increases, or as the magnitude of the dipole of the polar molecule increases.

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Dipole-induced dipole Interactions

- In the dipole–induced-dipole interaction, the presence of the partial charges of the polar molecule causes a polarization, or distortion, of the electron distribution of the other molecule (non-polar).
  - As a result, the second molecule acquires regions of partial positive and negative charge, and thus it becomes polar.

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Ion-induced dipole Interactions

- In the ion–induced-dipole interaction, the presence of positive/negative ions causes a polarization, or distortion, of the electron distribution of the other molecule (non-polar).
  - As a result, the non-polar molecule acquires regions of partial positive and negative charge, and thus it becomes polar.

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London Dispersion Interactions (Van der Waals Forces)

- Induced dipole between molecules.
- Acts between all types of molecules, polar or not.
- The London dispersion force is the weakest intermolecular force.
- The strength of these interactions within a given molecule depends directly on how easily the electrons in the molecules can move.

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- Dispersion is the principal force responsible for the existence of the condensed phases of certain molecular substances,
  - E.g. Benzene, other Hydrocarbons, Bromine, and the solid elements Phosphorus.

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Hydrogen Forces

- These bonds are generally stronger than ordinary dipole-dipole and dispersion forces, but weaker than true covalent and ionic bonds.

- Formed when H-atom of one molecule is attracted to a highly electronegative atom.

E.g. Between water molecules

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The phase rule

- The three primary phases (solid, liquid, and gaseous) of matter are often defined individually under different conditions,
  - But in most systems we usually encounter phases in **coexistence**.
  - For example, a glass of ice water on a sunny hot day comprises three coexisting phases: ice (solid), water (liquid), and vapor (gaseous).

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- The amount of ice in the drink depends heavily on several variables:
  - Amount of ice placed,
  - Temperature of the water, and
  - Temperature of the surrounding air.

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- The longer the drink is exposed to the warm air,
  - The more ice will melt (the amount of solid decrease), and
  - The more water will evaporate (the volume of liquid decrease)
- For this system, there is no establishment of equilibrium (??)

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- If the ice water is **sealed in a bottle**, evaporation effects are limited to the available headspace,
  - The ice melts to liquid, and evaporation becomes time and temperature dependent.
- If the container is placed in a **freezer**, only one phase, ice, may be present after long-term storage.
- **Heating** of the container, provided the volume stays fixed, could potentially cause the formation of only a vapor phase.
- **Opening and closing** of the container would change the vapor phase composition and thus affect equilibrium.

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- This one-component example can be extended to the two-component system of a drug suspension.
  - The suspended system will sit at equilibrium until the container is opened, and then equilibrium would have to be reestablished for the new system.
  - A new equilibrium or non-equilibrium state is established because dispensing of the suspension will decrease the volume of the liquid and solid in the container.
  - Therefore, a new system is created after each opening, dispensing of the dose, and then resealing.

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- **Gibbs phase rule**:
  - Each phase can be defined by a series of independent variables and their coexistence can only occur over a limited range.
  - Gibbs phase rule gives a relationship for determining -
    - The least number of intensive **variables** that can be **changed** without changing the equilibrium state of the system or alternately,
    - The least number required to define the state of the system.

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- This critical number is called F, the number of degrees of freedom of the system, and the rule is expressed as follows:

$$F = C - P + 2$$

- where C is the number of components and P is the number of phases present.

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- A phase can be defined as a homogeneous, physically distinct portion of a system that is separated from other portions of the system by bounding surfaces.
  - Thus, a system containing water and its vapor is a two-phase system.
  - An equilibrium mixture of (ice + liquid water + water vapor) is a three-phase system.
  - Two immiscible liquids (liquid water + oil) separated by a distinct boundary are counted as two different phases.

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- The number of components is the smallest number of constituents by which the composition of each phase in the system at equilibrium can be expressed in the form of a chemical formula or equation.

- The number of components in the equilibrium mixture of ice, liquid water, and water vapor is one.

  - The composition of all three phases is described by the chemical formula H_2O.

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- The number of degrees of freedom is the least number of intensive **variables** that must he fixed/known to describe the system completely.

- Although a large number of intensive properties are associated with any system, it is not necessary to report all of these to define the system.

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- For example, let us consider a given mass of a gas confined to a particular volume.
  - Using the phase rule only two independent variables are required to define the system (F = 1 - 1 + 2 = 2).
  - Because we need to know two of the variables to define the gaseous system completely, we say that the system has two degrees of freedom.
  - Therefore, it would be impossible for one to duplicate this system exactly unless the temperature, pressure, or another variable is known that may be varied independent of the volume of the gas.

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- Consider a system comprising a liquid, say water, in equilibrium with its vapor.
  - By stating the temperature, we define the system completely because the pressure under which liquid and vapor can coexist is also defined.
  - If we decide to work instead at a particular pressure, then the temperature of the system is automatically defined.
  - Again, this agrees with the phase rule ($F= 1 - 2 + 2 = 1$)

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- Suppose we cool liquid water and its vapor until a third phase (ice) separates out.
  - Under these conditions, the state of the three-phase ice-water-vapor system is completely defined, and the rule gives

$$F = 1 - 3 + 2 = 0.$$

  - In other words, there are no degrees of freedom.
  - If we attempt to vary the particular conditions of temperature or pressure necessary to maintain this system, we will lose a phase.

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- Thus, if we wish to prepare the three-phase system of ice-water-vapor, we have no choice as to the temperature or pressure at which we will work; **the combination is fixed and unique**.

- This is known as the critical point.

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- It is important to appreciate that as the number of components increases, so do the required degrees of freedom needed to define the system.

- Therefore, as the system becomes more complex, it becomes necessary to fix more variables to define the system.

- The greater the number of phases in **equilibrium**, however, the fewer are the degrees of freedom.

Table: Application of the Phase rule for one-component system

System	Number of Phases	Degree of Freedom	Comment
Gas, Liquid, or Solid	1	2	System is bivariate
Gas-Liquid, Liquid-Solid, or Gas-Solid	2	1	System is univariat
Gas-Liquid-Solid	3	0	System is invariat

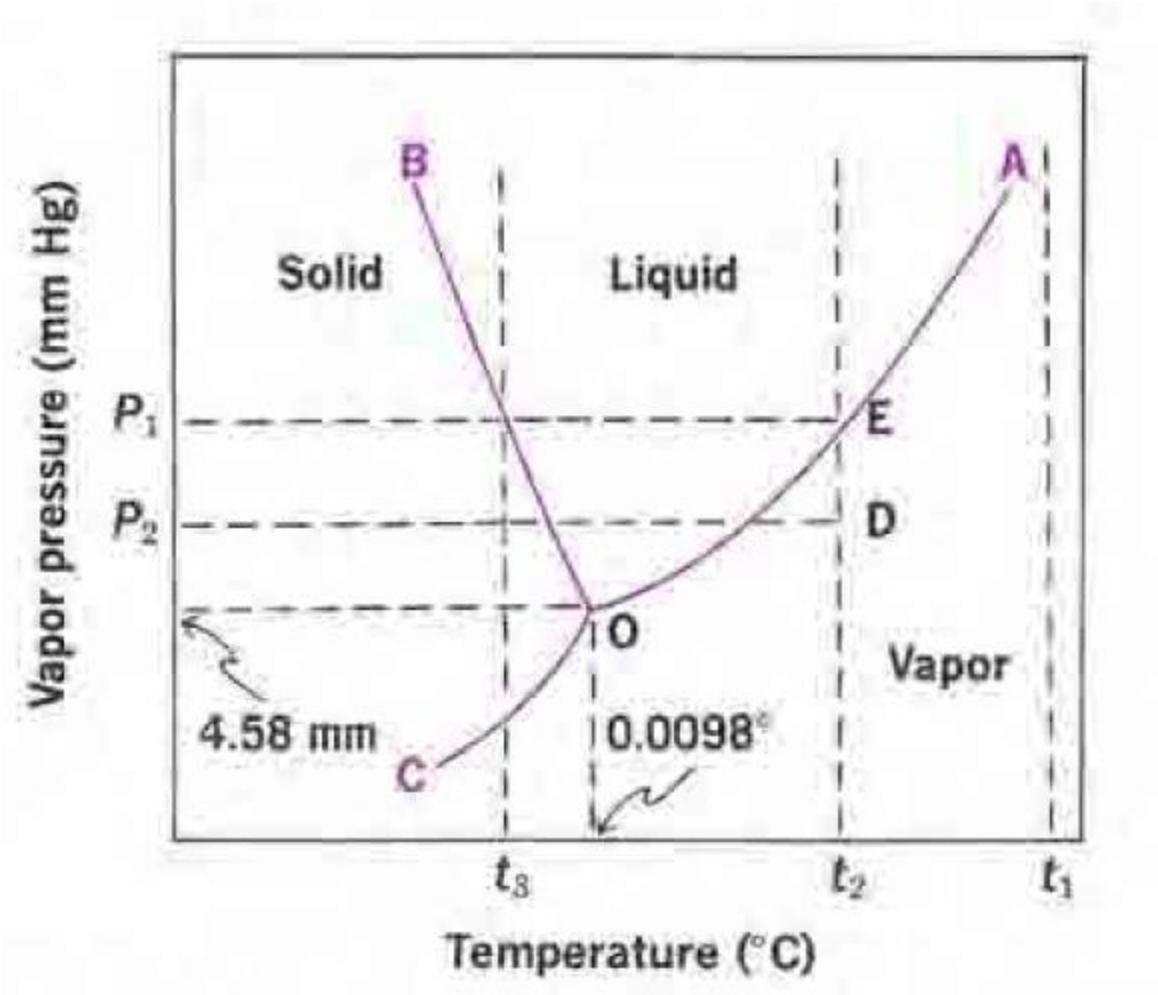

Fig. Phase diagram for water (one-component system) at moderate pressure.

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Two component (Binary) systems

- Two liquids can be completely miscible or completely immiscible depending their polarity.
  - Liquids with intermediate property are partially miscible.

E.g. Liquid water and phenol show limited miscibility below 70 ºC

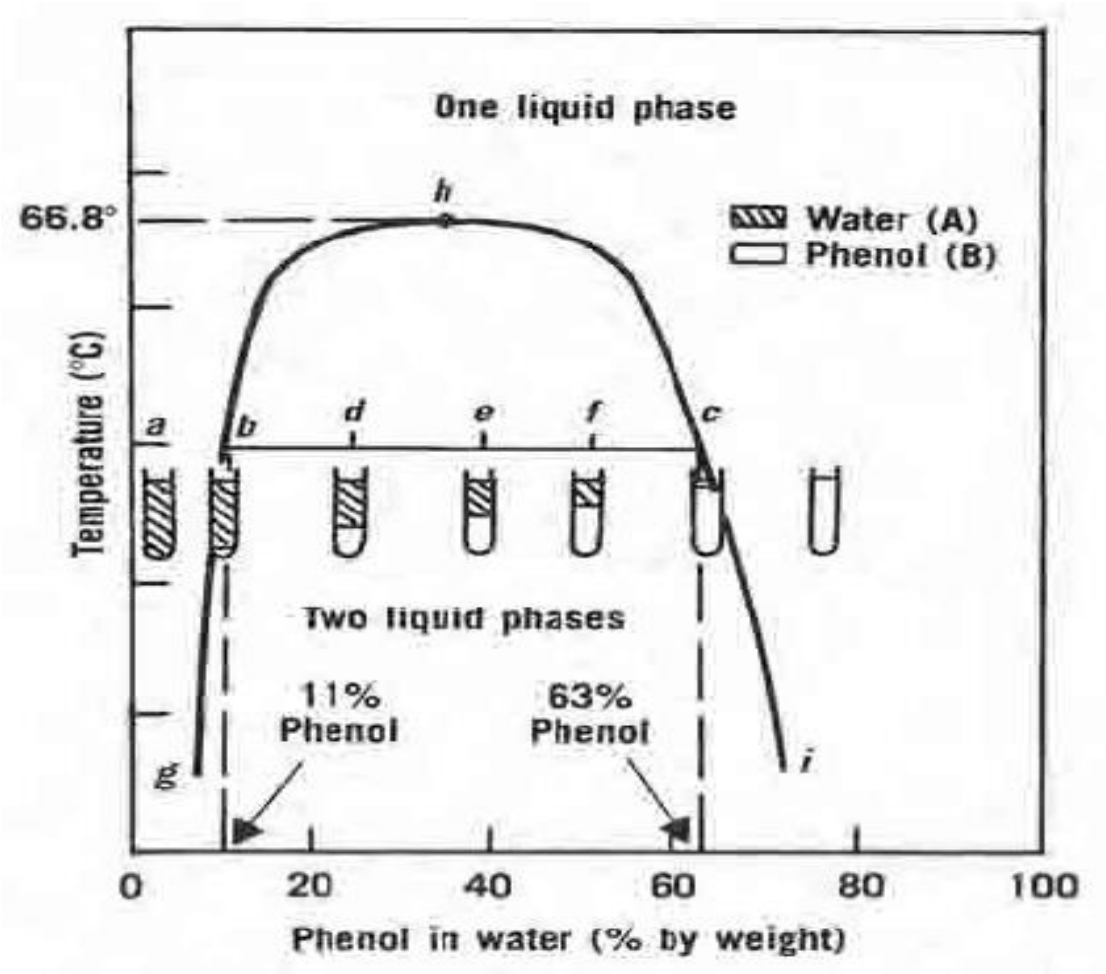

Fig. Phase diagram for phenol-water mixture (two-component system) under normal condition of atmospheric pressure.

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- As the diagram indicates, at low and high percentages of phenol, water and phenol mix completely, forming a single liquid phase.

- However, at intermediate compositions (and below the critical temperature) mixtures of phenol and water separate into two liquid phases.

  - Point "h" in the figure is the critical point.

  - Above the critical temperature, phenol and water are completely miscible

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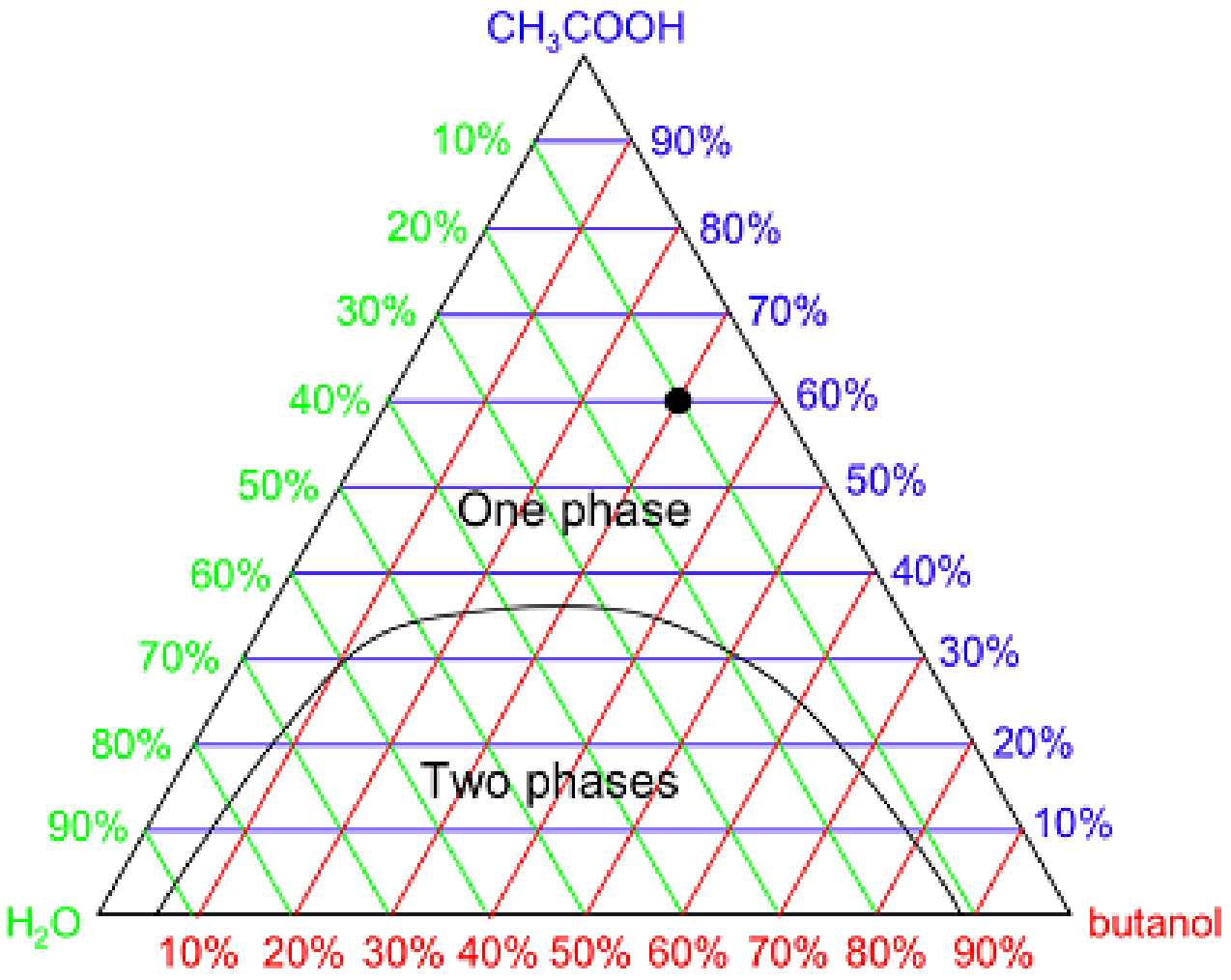
Three component (Ternary) systems

- Binary system plus one extra components.
- A system containing three components but only one phase.
- Since it is a three component system, triangular coordinate system (equatorial triangle graph) is used.


CH3COOH
10%
90%
20%
80%
30%
70%
40%
60%
50%
50%
One phase
60%
40%
70%
30%
80%
20%
Two phases
90%
10%
H2O
butanol
10% 20% 30% 40% 50% 60% 70% 80% 90%

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- There are different possible combination of adding the third component
  - If the 3rd component is soluble in only one of the two original liquids - mutual solubility of binary system will be decreased.
  - If the 3rd component has roughly the same solubility in both components, therefore mutual solubility will be increased